

A Novel Application of High-Carbon Fly-Ash as an Industrial Binder

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Industrial Binders

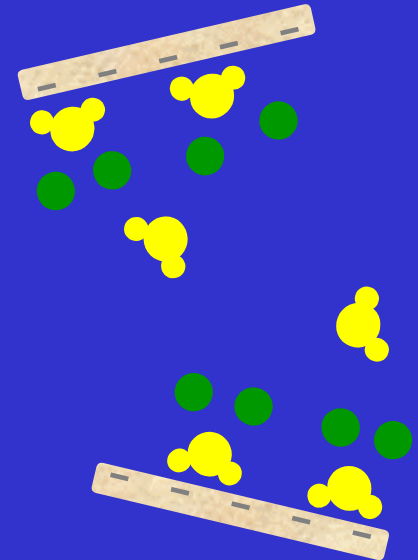
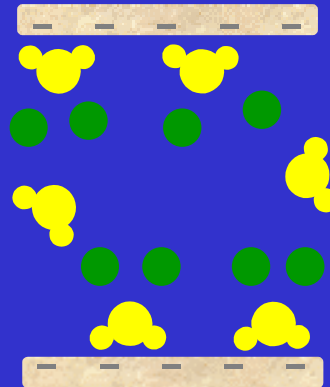
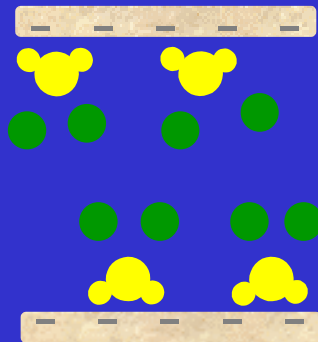
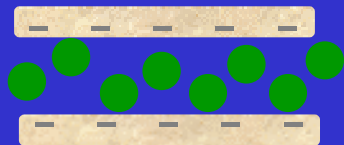
- There are numerous industrial applications where a binder is needed for agglomerating fine particulates
- Important applications include iron ore pelletization, particulate recycling, and molding sand for metal foundries
- Bentonite clay is currently the preferred binder.
- Bentonite production in 1999 was 3.85 million metric tons.
- 26% of this bentonite was used in foundry sands, and 16% in iron ore pelletization.
- Cost to the U. S. metal-casting industry was approximately \$43 million, and cost to the iron ore industry was approximately \$26 million.

Fly-Ash Binder

- There was no published work with fly-ash as a binder for this application
- Fly-ash as a binder is commonly used to partially replace portland cement in concrete
- Advantages
 - Low cost - Available from power plants located near steel mills - low cost (shipping alone can triple the cost of bentonite)
 - Environmental stewardship - 40 million tons of fly-ash is land filled in the U.S. each year

Bentonite dispersion

Sodium
Bentonite

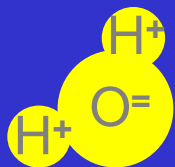
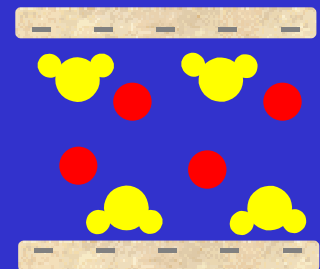
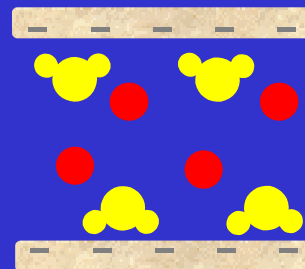
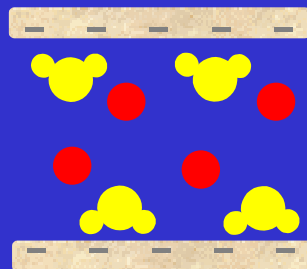
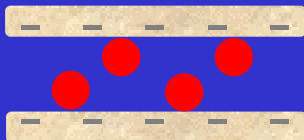


1

2

3

Calcium
Bentonite



Water



Na^+



Ca^{++}



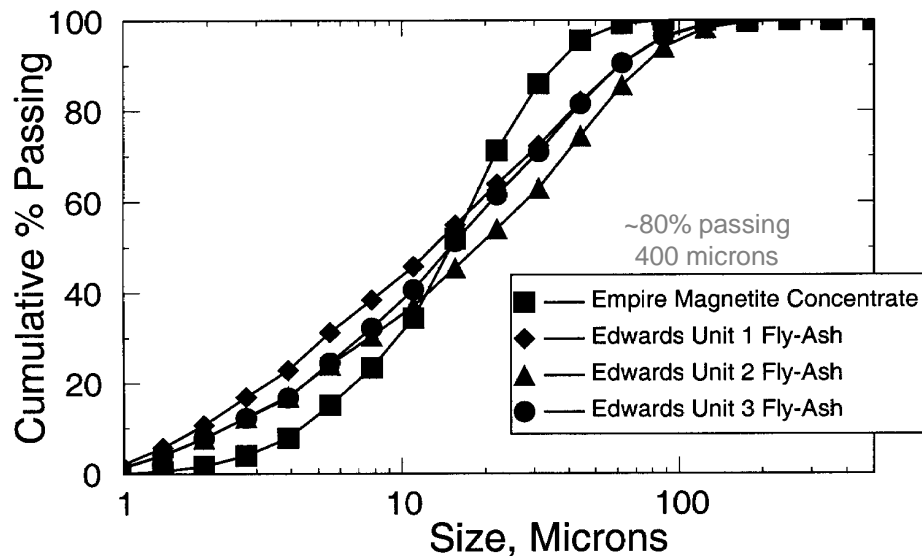
bentonite

Comparison of Bentonite to Fly-ash

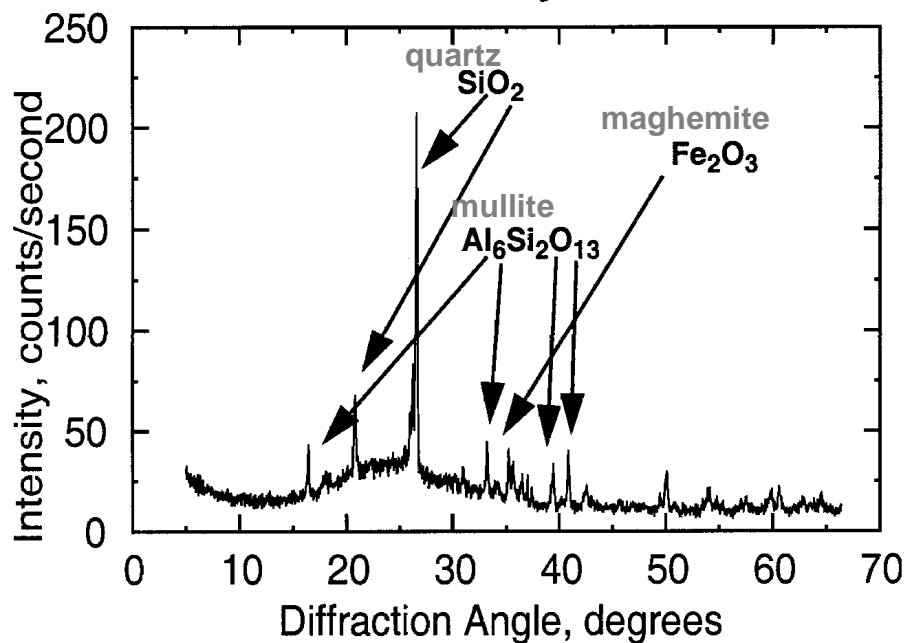
CRITERIA	BENTONITE	FLY-ASH
Primary constituents	SiO_2 , Al_2O_3 , Fe_2O_3	SiO_2 , Al_2O_3 , Fe_2O_3
Structure	Crystalline	amorphous
Dry particle size	80% -74 μm ; 60% -325 μm (-1 μm crystals)	80% -50 μm
Expandable/ absorbent/ dispersive	yes	no
bonding	Physical/gel	Chemical/ pozzolanic

Analyte	Unit 2 Fly-Ash, %	Bentonite, %
SiO ₂	38.68	34.62
Al ₂ O ₃	22.81	23.16
Fe ₂ O ₃	6.06	5.49
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃	67.55	68.26
CaO	15.04	9.63
MgO	3.54	2.11
Na ₂ O	1.70	1.06
K ₂ O	0.94	0.39
TiO ₂	1.17	1.25
MnO ₂	0.05	0.01
P ₂ O ₅	0.91	2.20
SrO	0.20	0.39
BaO	0.48	0.53
SO ₃	1.19	5.93
LOI	7.27	13.24

Microtrac Size Analyses



Unit 2 Fly-Ash



ASTM Classification of Fly Ashes

ASTM C618-98	Class F	Class C
$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, min. %	70.0	50.0
SO_3 , max. %	5.0	5.0
Moisture content, max. %	3.0	3.0
Loss on Ignition, max. %	6.0 (12.0)	6.0

Fly-Ash Based Binders

- Fly-ash must undergo a pozzolanic reaction to act as a binder, which requires the presence of alkali and water.
- Pozzolanic reactions tend to be slow (several days), and binder applications require fast binding
- Fly-ash based binders are made from fly-ash, calcium hydroxide, and accelerator (soluble calcium salts)

Iron Ore Pellet Production

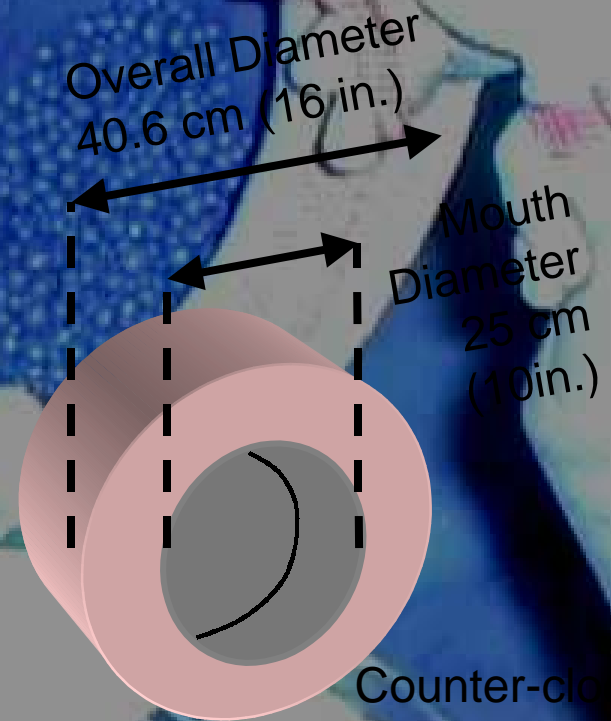
- Pellets are produced by combining iron ore concentrate at approximately 10% moisture with a small amount of binder, and tumbling in a pelletizing drum or disk. Pellets are then fired at 1200 C .
- Pellets are approximately 1.2 cm in diameter, and before firing they must have a “green strength” > 22 N/pellet

Carbon Content in Pellets

- Carbon content of the fly-ash does not reduce the strength of pellets, and can even increase the strength slightly.
- Carbon will act as a supplemental fuel during pellet firing, and will therefore be beneficial for pellet production.

Pelletization Procedure

- Kneader mix binder into 3kg concentrate at 350 rpm & 150 rpm orbital motion for various times
- Delump with 2.4mm (8 mesh) screen
- Add some feed and make-up water spray to balling drum, form seeds, periodically screen, and grow into 12.7 x 11.2 mm (1/2 x 7/16 in.) Diameter pellets
- Test 20 pellets each for wet knock and wet compressive strength
- Dry at 105°C
- Metallographic preparation for SEM



**Balling Drum
Schematic**

Testing Procedures

Test	Procedure	Use of Data
Wet-Knock	Undried pellets were dropped repeatedly from 46 cm (18 in.) onto a steel plate. The number of drops required for fracture was recorded.	Measures the ability of the wet pellet to remain intact during handling.
Wet-Crush	Undried pellets were crushed using an Instron compression machine, with a crosshead speed of 40 mm/min. The fracture load was recorded.	Measures the ability of the wet pellet to remain intact during handling.
Dry-Crush	Pellets dried at 105°C (221°F) for at least 1 hour were then crushed using an Instron 4206 compression test machine. Ultimate strength was recorded.	Measures the ability of dried pellets to survive handling and firing (> 22.2 newtons).

Statistical Data Analysis

- Each datum is the average of 20 values
- The error bars show the 95% confidence interval calculated according to:

$$P_{95} = \left(\frac{t_{95}(19)}{\sqrt{\hat{I}}} \right) = \pm(0.386)s$$

- Each experiment was repeated at least once and all P_{95} values overlapped initial values

s = measured standard deviation for the data set

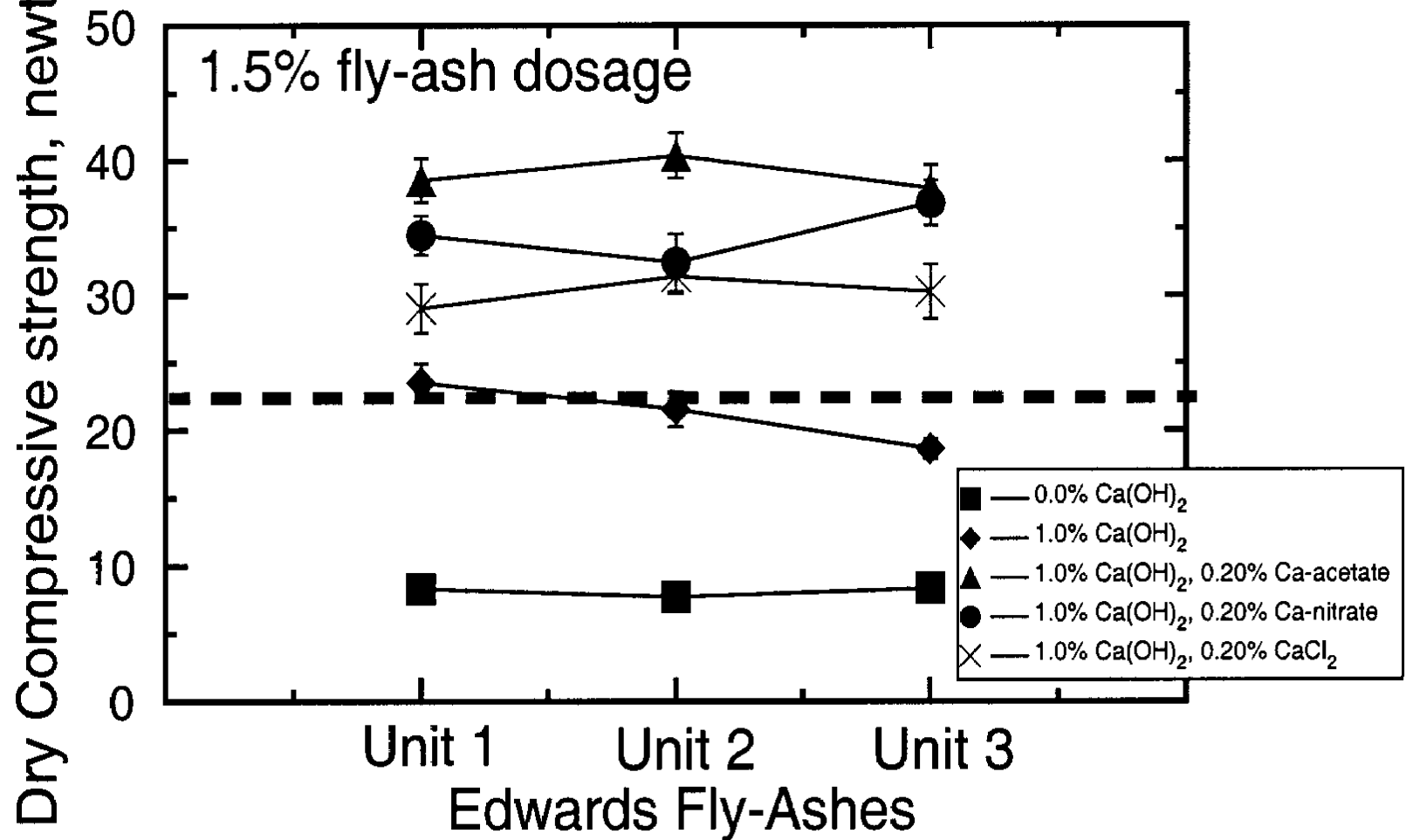
N = number of data points

$T_{95}(19)$ = the t-value for the 95% confidence interval , at 19 degrees of freedom

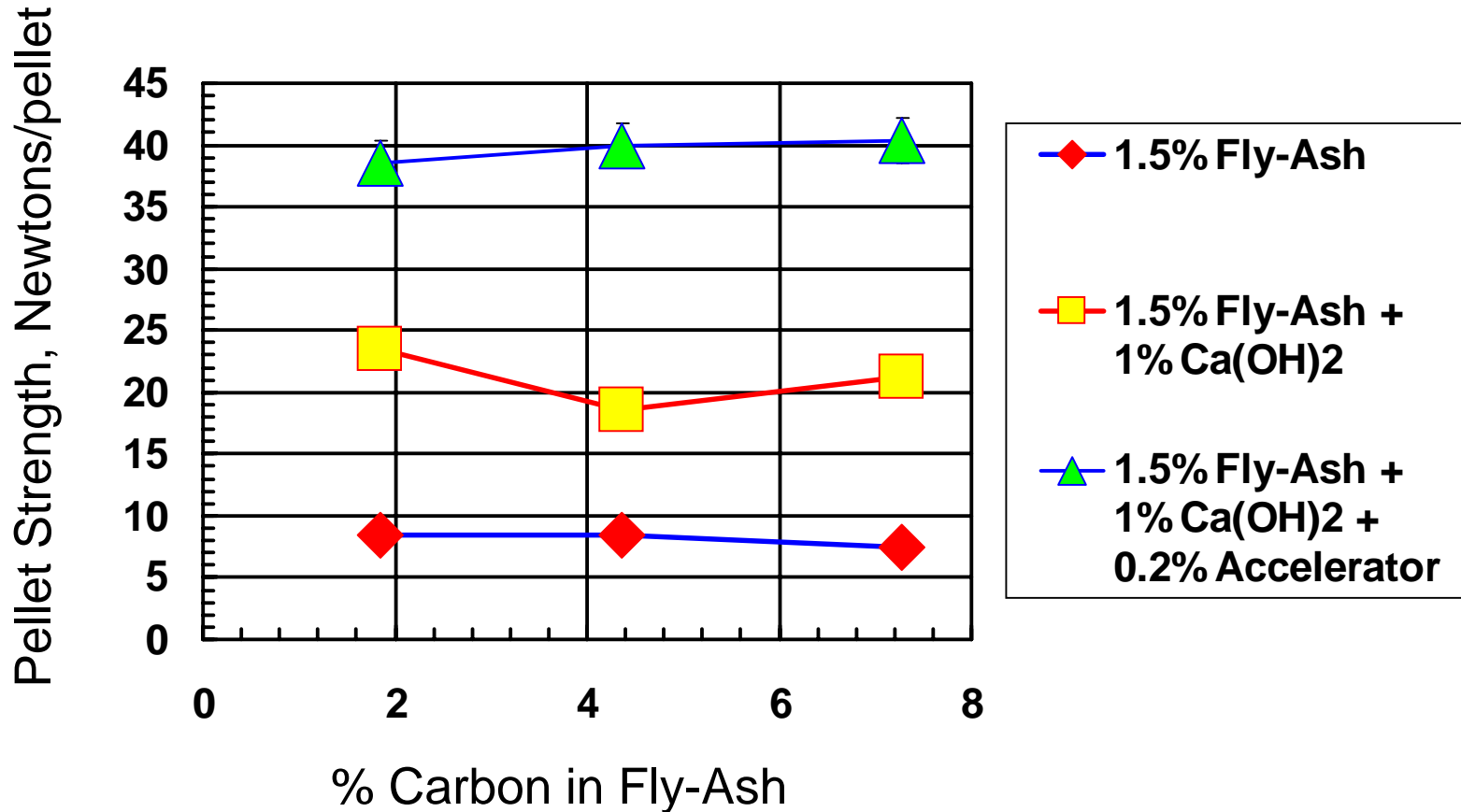
Why Add Activator and Accelerator to Fly-ash?

- Lime (CaO) or Ca(OH)_2 is added as an activator to induce pozzolanic reactivity (cementitious)
- Compounds, such as calcium acetate, calcium nitrate, or calcium chloride were added to accelerate the pozzolanic reaction because:
 - The activator has higher solubility in the CaCl_2 solution than in water alone
 - CaCl_2 adds calcium ion, increasing formation of the bonding calcium silicates
 - CaCl_2 is hygroscopic (absorbs/retains water), allowing the reaction to proceed longer

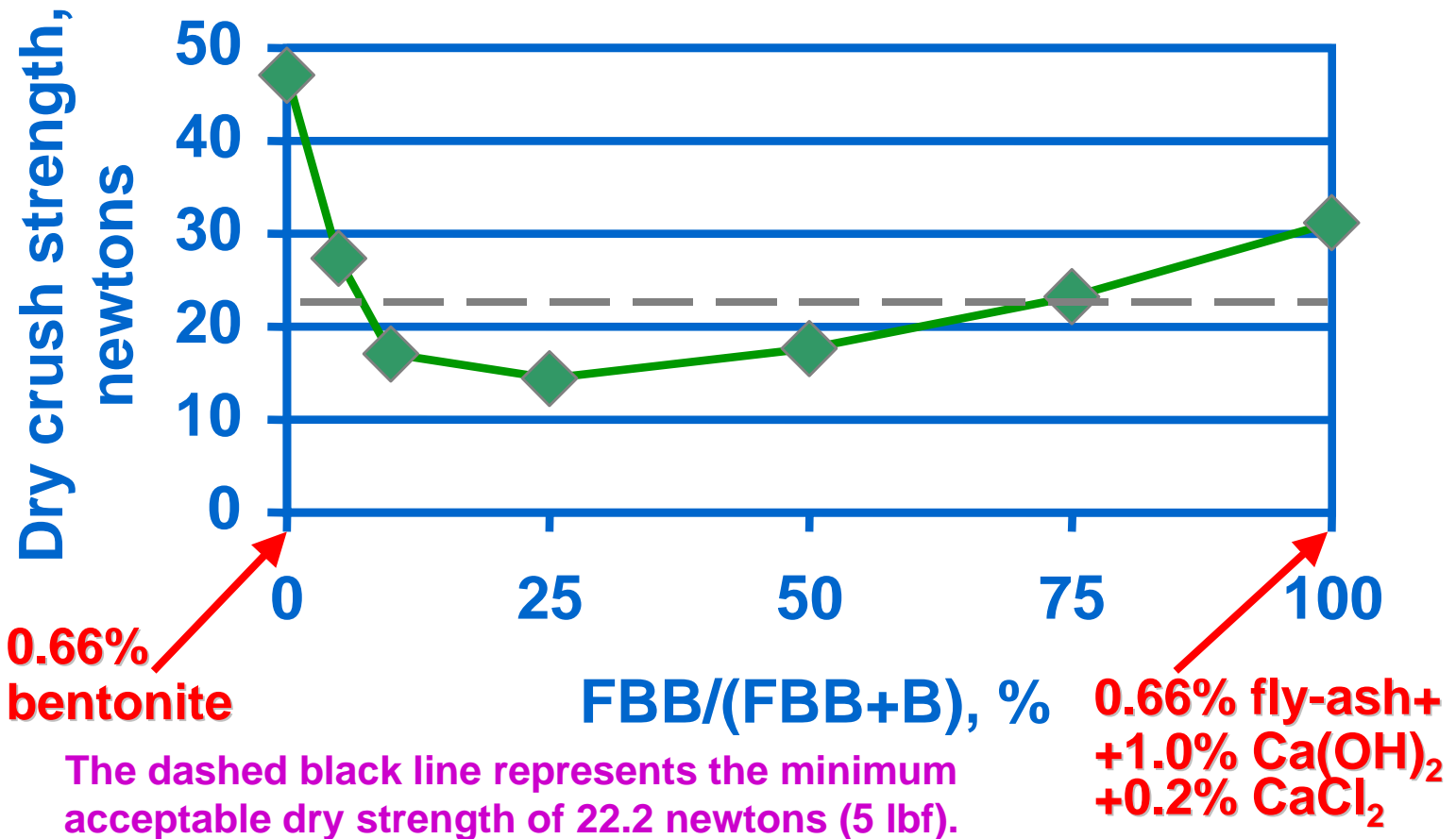
Accelerators for Fly-Ash Binders



Pellets made with fly-ash binders of varying carbon content



Strength of dry iron ore pellets at varying mixtures of fly-ash based binder (FBB) and bentonite (B).



Compatibility of Fly-Ash-Based Binder with Bentonite Binder

- Fly-ash based binder gives strengths only slightly lower than a similar dosage of bentonite.
- Mixtures of fly-ash and bentonite do not perform as well as either bentonite alone, or fly-ash alone.
- Incompatibility is apparently due to the difference in binding mechanism between the two binders (physical vs. pozzolanic)

Steel Plant Waste

- 50,000 tpy desulfurization slag landfilled at one steel plant
- The slag is rich in iron and should not be landfilled
- Goals:
 - Recover the iron units
 - Save money
 - Environmental stewardship
- Recycle the slag concentrate by pelletizing it into blast furnace feedstock

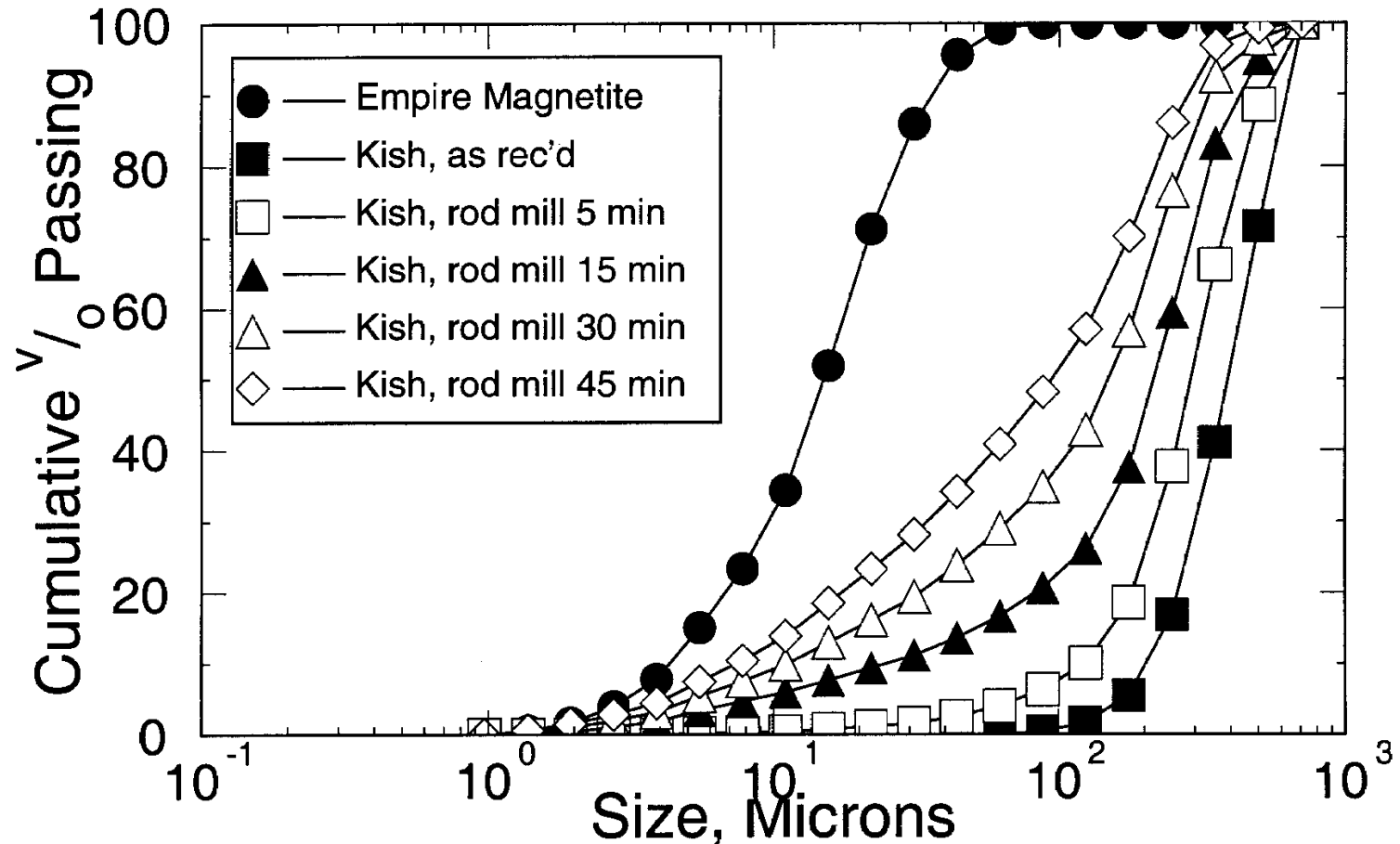
Chemical	Slag concentrate, Wt%
% of Head Wt.	27.0%
Fe, Total	61.7
Fe, Metal	55.0
FeO	8.6
CaO	17.2
MnO	0.1
SiO ₂	9.8
MgO	2.3
Na ₂ O	0.1
Al ₂ O ₃	2.2
C	4.2
S	2.1
Total	101.6

Slag Concentrate Pellet Production

- Steelmaking slags contain recoverable iron, both as metal and as iron oxide.
- Iron concentrated from slag is a powder that is unsuitable for recycle to the steelmaking operation.
- Concentrates produced from slag must be pelletized so that they can be handled and recycled.
- Pellet properties are sensitive to particle size distribution of the slag concentrate and to the type and dosage of binder used.

Steel Plant Waste

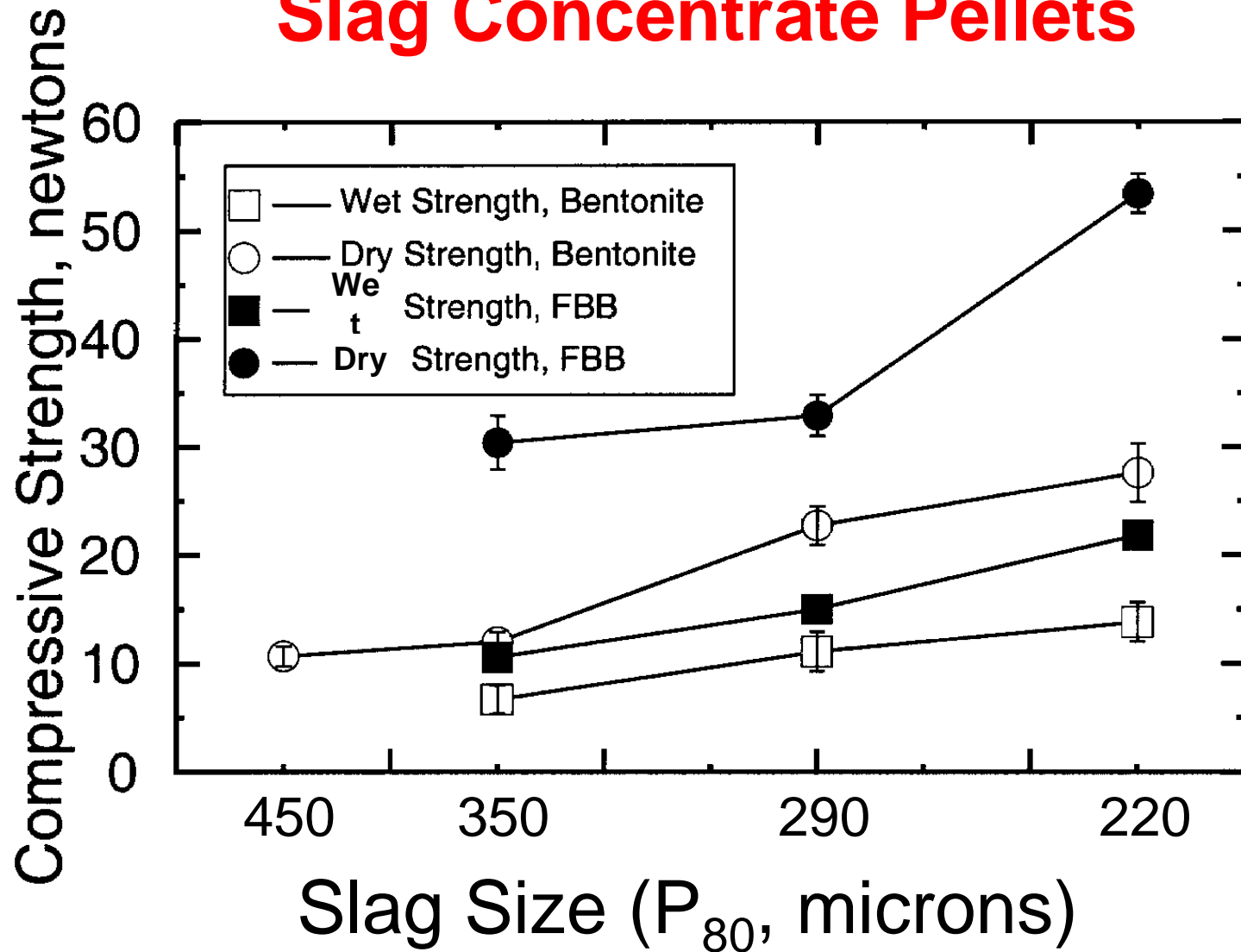
Ferrous Concentrate Size Analyses



Slag Concentrate Pellets

Binder	P ₈₀ , microns	Wet knock, number of drops	Wet crush, newtons (lbf)	Dry crush, newtons (lbf)	Sintered crush, newtons (lbf)
bentonite	450	not determined	not determined	10.7+/-0.9 (2.4+/-0.2)	1041+/-334 (234+/-75)
bentonite	350	4.6+/-0.5	6.7+/-1.3 (1.5+/-0.3)	12.0+/-0.9 (2.7+/-0.2)	1072+/-356 (241+/-80)
bentonite	290	13.9+/-1.1	11.1+/-1.8 (2.5+/-0.4)	22.7+/-1.8 (5.1+/-0.4)	1806+/-444 (406+/-100)
bentonite	220	7.4+/-0.3	13.8+/-1.8 (3.1+/-0.4)	27.6+/-2.7 (6.2+/-0.6)	1832+/-374 (412+/-33)
FBB	220	7.4+/-0.8	22.2+/-1.3 (5.0+/-0.3)	53.4+/-1.8 (12+/-0.4)	1378+/-222 (310+/-50)

Slag Concentrate Pellets



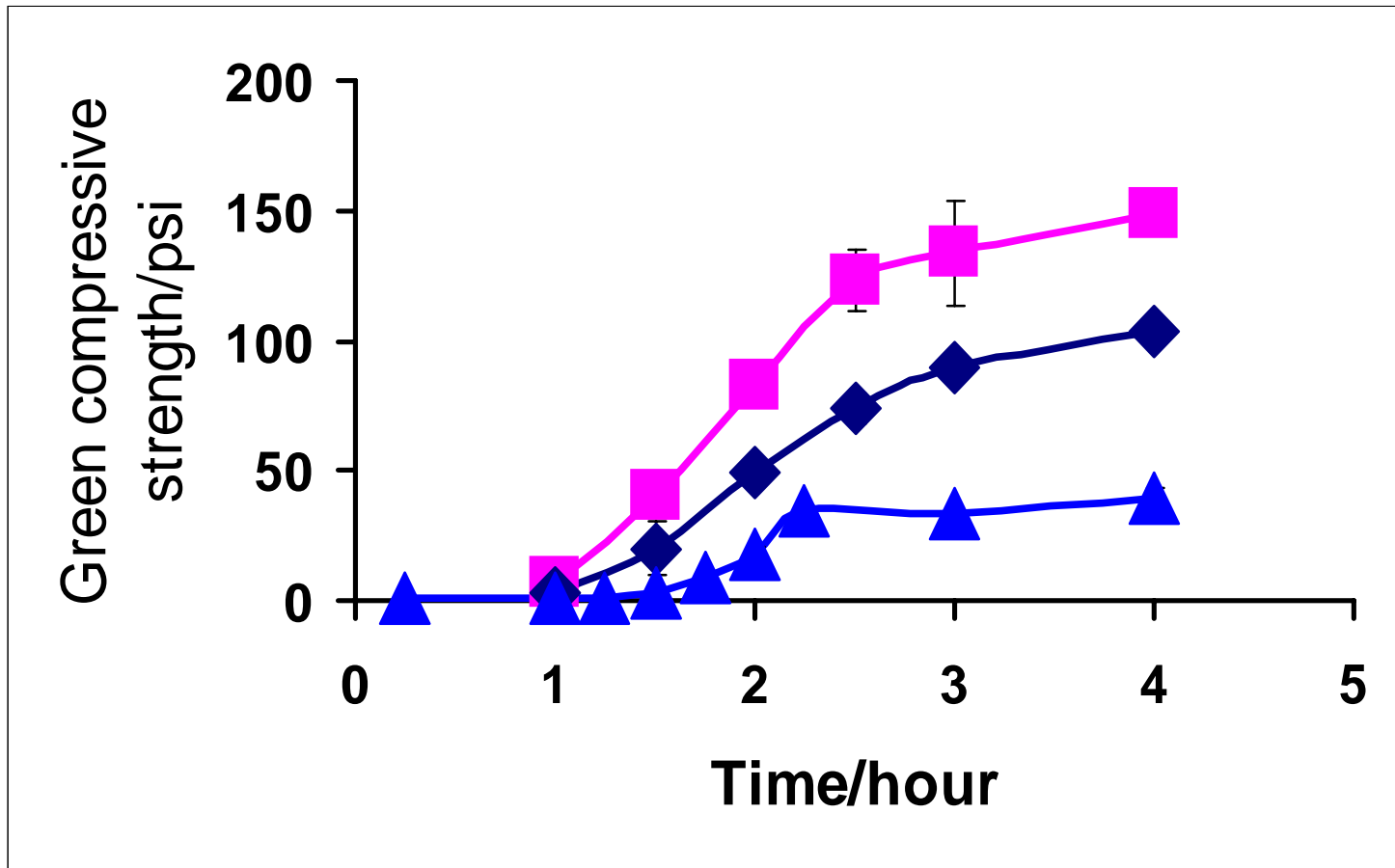
Foundry Sand Binder

- Foundries currently use bentonite for binding together sand grains to make metal-casting molds.
- They consumed approximately 1 million tons of bentonite in 1999, valued at \$43 million.
- Carbon is a useful additive in foundry molds, and so high-carbon fly-ash-based binders would be well suited to this application.

Foundry Sand Test Specimens

- To produce test specimens:
 - Sand is mixed with water and binder
 - Mixture is compacted under controlled conditions to produce a cylinder 2 in. tall and 2 in. diameter
- Specimens are compressed to determine strength.
- A Class C fly-ash was used for these experiments, as it does not require additives to act as a binder.

Compressive Strength vs. Curing Time



■ 15% flyash

◆ 10% flyash

▲ 6.5% flyash

Conclusions

- Fly-Ash Based Binder (FBB) has performance comparable to that of bentonite.
- Good quality FBBs can be made using high-carbon fly-ashes. The presence of carbon is often beneficial in binder applications.
- FBB and bentonite binders appear to be fundamentally incompatible with each other, due to their very different binding mechanisms
- Steel plant desulfurization slag concentrate could be pelletized for recycle using FBB, provided that it was ground to a fine enough size to produce acceptable pellets.
- Foundry sand can be bonded using FBB provided that sufficient curing time is allowed.

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